

Syntheses and Characterizations of Metal-Organic Frameworks with Unusual Topologies Derived from Flexible Dipyridyl Ligands

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Two flexible *exo*-bidentate ligands, 2,2'-bis(3-pyridylmethylenoxy)-1,1'-biphenylene (3,3'-bpp) and 2,2'-bis(4-pyridylmethylenoxy)-1,1'-biphenylene (4,4'-bpp), were synthesized and employed for the preparation of coordination polymers. Seven metal-organic complexes, $[\text{Zn}_2(3,3'\text{-bpp})_2\text{Cl}_4]$ (**1**), $[\text{Zn}_2(3,3'\text{-bpp})_2\text{Br}_4]$ (**2**), $[\text{Zn}(4,4'\text{-bpp})\text{Cl}_2]_n$ (**3**), $[\text{Zn}(4,4'\text{-bpp})\text{Br}_2]_n$ (**4**), $[\text{Co}(4,4'\text{-bpp})_2(\text{SCN})_2]_n$ (**5**), $[\text{Cd}(4,4'\text{-bpp})_2(\text{SCN})_2 \cdot 2\text{H}_2\text{O}]_n$ (**6**) and $[\text{Cd}(4,4'\text{-bpp})(\text{dca})_2]_n$ (**7**) ($\text{dca}^- = \text{dicyanamide}$), have been obtained through self-assembly reactions of 3,3'-bpp or 4,4'-bpp with the divalent metal ions Zn^{II} , Co^{II} and Cd^{II} . Crystal structure analyses reveal that **1** and **2** are dinuclear metallomacrocycles, are isomorphous and possess a layer network built from metallomacrocycles through π - π interactions. In drastic contrast, **3** and **4** exhibit a three-dimensional structure consisting of one-dimensional polymeric chains held together through π - π interactions between adjacent pyridyl rings.

The metal-organic frameworks of **5**, **6**, and **7** possess unusual topologies: Complex **5** is a two-dimensional polymer based on folded rectangular boxes and zigzag chains, whereas **6** is a polycatenated species consisting of inclined interpenetrating two-dimensional layers, and each layer is constructed by the alternating assembly of left-hand (*M*) and right-hand (*P*) cylindrical 2_1 helices. In **7**, dca^- connects Cd^{II} centers forming a two-dimensional $[\text{Cd}(\text{dca})_2]_n$ layer, which is fused with (*M*)- and (*P*)- Cd -(4,4'-bpp) helical chains into a three-dimensional structure. The results suggest that the nature of organic ligands and the coordination preferences of transitional metal ions have a great influence on the structures of metal-organic complexes.

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Introduction

Metal-directed self-assembly of organic ligands and metal ions, or organometallic moieties, to form well-defined structures has been a very attractive field in recent years.^[1–6] The increasing interest in this field is justified not only by the intellectual challenge in controlling and manipulating the self-assembly process,^[3,4] but also by their fascinating structural diversities and potential application in functional materials, nanotechnology and biological recognition.^[5,6] In this context, novel supramolecular topologies with various sizes and shapes of channels or cavities can be controlled and tuned through judiciously selecting assembly-influencing factors, such as structural characteristics of polydentate organic ligands,^[7,8] the coordination

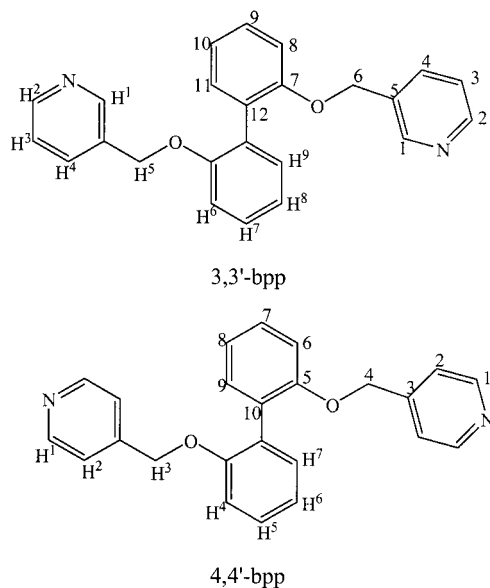
nature of the metal ions,^[9] counter anions,^[10] the metal/ligand ratio,^[11] and solvent system.^[12] So far, of diverse elegant efforts to find the key factors in the course of the construction of metal-based supramolecules, the dominant and most efficient synthetic strategy is the employment of various organic ligands as molecular building blocks or tectons. Among these organic ligands, one of the most fruitful choices has been the use of neutral pyridyl-containing bidentate or multidentate organic building blocks, owing to their simple bridging mode and strong coordination ability to transition-metal ions. Rigid, rod-like, *exo*-bidentate ligands, such as 4,4'-bipyridine (4,4'-bipy),^[13,14] are suitable examples of tectons that have been used often for the rational design of solid-state architectures of coordination polymers. Moreover, structures containing larger holes can potentially be built by using longer rigid connectors between the pyridyl rings. For example, Fujita et al. have reported a series of two-dimensional square frameworks with different sizes upon increasing the number of phenyl rings between the pyridyl rings.^[15] Compared to rigid bridging ligands, flexible bridging tectons can produce some unique frameworks with beautiful aesthetics and useful properties because of their flexibility and conformational freedom.^[16] However, owing to the difficulty in predicting the structures of the products, the rational design of coordination poly-

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mers from flexible ligands is still a formidable challenge.^[17]

In our previous studies we prepared a series of flexible organosulfur ligands by connecting (methylsulfanyl)pyridyl or -pyrimidyl groups to aromatic ring spacers.^[18–21] Assembly of such flexible tectons and metal ions resulted in several unique structural motifs, such as a metallosupramolecular cube,^[18] a one-dimensional nanotube,^[19] square rings with guest molecules,^[20] and two-dimensional crown-like structures.^[20,21] Considering the geometric requirement of symmetry and stereochemistry, and with the aim of investigating the effects of distortion of the connector in the dipyrindyl ligands on the assembly process and products, we have introduced a biphenyl connector into the reaction system and prepared two more flexible ligands, 2,2'-bis(3-pyridylmethylenoxy)-1,1'-biphenylene (3,3'-bpp) and 2,2'-bis(4-pyridylmethylenoxy)-1,1'-biphenylene (4,4'-bpp), in which the distortion of the biphenyl connector can endow the metal-organic frameworks with unique structural and functional properties.^[22] Moreover, metal-organic complexes with a biphenyl connector can be used as simple probes for the investigation of chiral complexes derived from 1,1'-bi-2-naphthol.^[23,24] Herein, we wish to report the syntheses and characterizations of two metallomacrocyclic complexes based on 3,3'-bpp — $[\text{Zn}_2(3,3'\text{-bpp})_2\text{Cl}_4]$ (**1**) and $[\text{Zn}_2(3,3'\text{-bpp})_2\text{Br}_4]$ (**2**) — and five novel coordination polymers based on 4,4'-bpp — $[\text{Zn}(4,4'\text{-bpp})\text{Cl}_2]_n$ (**3**), $[\text{Zn}(4,4'\text{-bpp})\text{Br}_2]_n$ (**4**), $[\text{Co}(4,4'\text{-bpp})_2(\text{SCN})_2]_n$ (**5**), $[\{\text{Cd}(4,4'\text{-bpp})_2(\text{SCN})_2\} \cdot 2\text{H}_2\text{O}]_n$ (**6**), and $[\text{Cd}(4,4'\text{-bpp})(\text{dca})_2]_n$ (**7**) ($\text{dca}^- = \text{dicyanamide}$).



Result and Discussion

Synthesis and Characterization

The ligands 3,3'-bpp and 4,4'-bpp are readily prepared from commercially available 2,2'-biphenol and 3-picolyl

chloride hydrochloride or 4-picolyl chloride hydrochloride in the presence of NaOH by a convenient method. The ligands are soluble in most solvents, except for water. Treatment of 3,3'-bpp with ZnCl_2 or ZnBr_2 in a 1:1 molar ratio in MeOH/ H_2O for several hours produced large amounts of white precipitates of **1** and **2**, respectively, in quantitative yield. The elementary analysis results are consistent with dinuclear metallomacrocycles of formula $\text{Zn}_2(3,3'\text{-bpp})_2\text{Cl}_4$ and $\text{Zn}_2(3,3'\text{-bpp})_2\text{Br}_4$, respectively. Compounds **1** and **2** are poorly soluble in common solvents except for DMF and DMSO. Hence, ^1H NMR spectra were recorded in $[\text{D}_6]\text{DMSO}$; the results confirmed the proposed formula, displaying a symmetric pattern.

It is well known that the relative orientation of coordination sites in organic ligands is also one of the most important factors for controlling the construction of supramolecular architectures. Hence, it is expected that the relative different orientation of the nitrogen donors in the pyridyl rings might lead to unusual building blocks, whose assembly with metal ions can produce unique structural frameworks. Indeed, assembly of 4,4'-bpp with ZnCl_2 or ZnBr_2 in a 1:1 molar ratio generated the one-dimensional polymeric chain complexes **3** and **4**. The directed reaction of 4,4'-bpp and ZnCl_2 or ZnBr_2 in MeOH/ H_2O afforded precipitates that are not soluble in any solvents. The MeOH solution of ZnCl_2 or ZnBr_2 , affording crystals suitable for X-ray single-crystal diffraction. Compounds **3** and **4** are insoluble in most common solvents. It is noteworthy that the Zn^{II} centers in **1–4** adopt a distorted tetrahedral coordination geometry, with two halide counteranions coordinating to a metal center as terminal ligands, preventing the formation of extended frameworks. This prompted us to choose either a metal ion with a high coordination number or bridging counteranions. Co^{II} and Cd^{II} are known to be usually six-coordinate with an octahedral geometry in their pyridyl-containing $\text{Co}(\text{SCN})_2$ ^[25] and $\text{Cd}(\text{SCN})_2$ ^[26] complexes. Reactions of 3,3'-bpp with Co^{II} and Cd^{II} with different counteranions failed to generate desirable single crystals, but we succeeded in the isolation of **5** and **6** by assembly of 4,4'-bpp with $\text{Co}(\text{SCN})_2$ and $\text{Cd}(\text{SCN})_2$ under the same reaction conditions. Interestingly, the metal centers demonstrate a similar coordination environment and the ligands possess the same coordination mode, although **5** and **6** represent two distinctly different structural motifs. Upon introducing the bridging dca^- ligand^[27,28] into the reaction system, the three-dimensional complex **7**, consisting of $\text{dca}-\text{Cd}$ layers and $\text{Cd}-(4,4'\text{-bpp})$ helical chains, was successfully isolated.

In the IR spectra of complexes **1–7**, the absorption bands of the skeletal vibrations of the aromatic rings appear in the $1420\text{--}1630\text{ cm}^{-1}$ region. The $\text{C}\equiv\text{N}$ stretching vibration of the thiocyanate group in **5** and **6** appears as a single and very strong peak at 2075 and 2030 cm^{-1} , respectively, similar to those found in thiocyanate-*N* coordination.^[24,25] The IR spectrum in complex **7** displays strong absorption bands in the $2170\text{--}1305\text{ cm}^{-1}$ region, indicating the presence of $\text{C}\equiv\text{N}$ of dca^- .^[27,28]

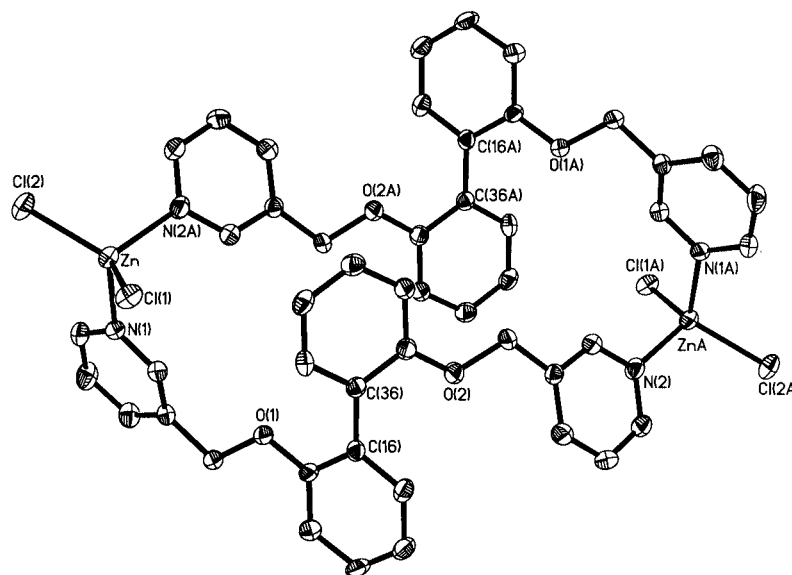


Figure 1. Molecular structure of complex **1** with the thermal ellipsoids at 30% probability level

Structural Description

[Zn₂(3,3'-bpp)₂Cl₄] (**1**)

The single-crystal X-ray diffraction analysis of **1** shows a neutral, dinuclear, metallacyclic structural motif with the Zn^{II} having a distorted tetrahedral geometry. As shown in Figure 1, each Zn^{II} is coordinated by two nitrogen atoms from different 3,3'-bpp and two terminal Cl[−] ions. The Zn–N bond lengths are in the range 2.061(4)–2.070(5) Å, which are typical values for Zn^{II}–N_{py} coordination distances.^[29] The Cl(1)–Zn–Cl(2) bond angle [123.52(7)°] is larger than the N(1)–Zn–N(2A) bond angle [99.53(18)°], probably in order to minimize Cl⋯Cl interactions. The dihedral angle between the two pyridyl rings attached to Zn^{II} is 83.2°, which means that they are approximately perpendicular; 3,3'-bpp acts as an *exo*-bidentate ligand, where the pyridyl rings are slightly twisted with respect to the corresponding linking phenyl rings, with the dihedral angles between them being 24.7° and 26.5°, respectively. The two phenyl rings about the central bond have a drastic twisting, with the dihedral angle between them being 130.5°. The combination of these twistings allows 3,3'-bpp to link ZnCl₂ units into a dinuclear metallacycle. The Zn⋯Zn separation in the cycle is 14.015 Å, which is longer than in known zinc macrocycles.^[29] Owing to the high distortion and flexibility of 3,3'-bpp, no enclathration of guest molecules is observed in **1**. There are no other noteworthy weak interactions between the adjacent macrocycles. Interestingly, every macrocycle has significant π – π interactions with its four closet neighbors. As shown in Figure 2, one phenyl ring of 3,3'-bpp and one pyridyl ring from the adjacent macrocycle are approximately parallel, with the dihedral angle between them being 24.7° and the distance between their centroids being 4.155 Å,^[31] resulting in the formation of one-dimensional stacked macrocycles; the other phenyl ring of 3,3'-bpp and one phenyl ring from another adjacent

macrocycle are completely parallel, with the distance between their centroids being 3.922 Å, further producing a layered network formed by stacked macrocycles.^[32]

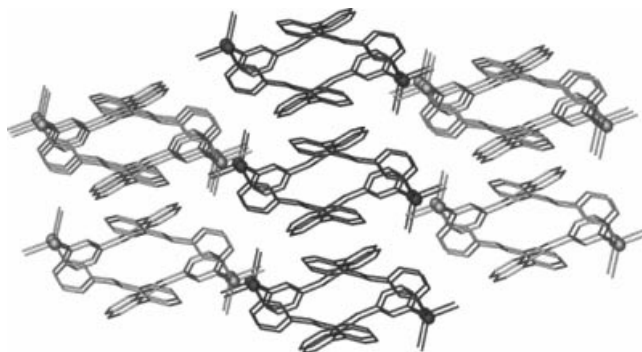


Figure 2. View of packing structure along *a* axis in **1** showing that there are no other interactions between adjacent macrocycles

[Zn₂(3,3'-bpp)₂Br₄] (**2**)

Compounds **1** and **2** are isomorphous, which suggests that the Br[−] and Cl[−] counteranions have no effect on the formation of the metallomacrocycle. As shown in Figure 3, Zn^{II} is coordinated by two nitrogen atoms from different 3,3'-bpp ligands and two terminal Br[−] ligands in a distorted tetrahedral geometry. The Zn–N bond lengths and the N–Zn–N bond angle are 2.068(8)–2.085(9) Å and 98.6(3)°, respectively, similar to those in **1**. The dihedral angle of the two pyridyl rings coordinated to Zn^{II} is 81.0°. In the *exo*-bidentate 3,3'-bpp ligand, the dihedral angles between the two phenyl rings as well as between the phenyl rings and their corresponding linking pyridyl rings are 130.2, 28.5 and 26.1°, respectively. Thus, 3,3'-bpp connects ZnBr₂ units forming a dinuclear metallomacrocycle with a Zn⋯Zn separation of 14.113 Å. Similar to **1**, π – π interactions between every macrocycle and its four adjacent

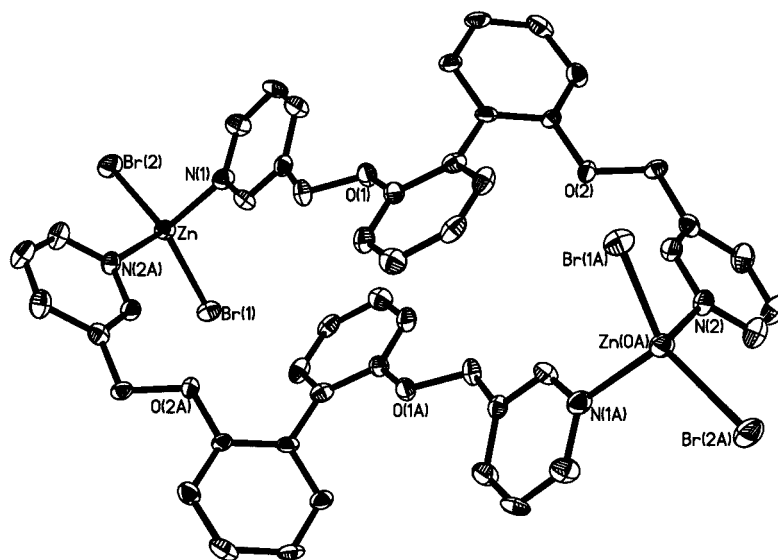


Figure 3. Molecular structure of complex **2** with the thermal ellipsoids at 30% probability level

macrocycles further stack it into a layered network structure.

$[\text{Zn}(\text{4,4'}\text{-bpy})\text{Cl}_2]_n$ (**3**)

The single-crystal X-ray structural analysis reveals that **3** is a one-dimensional zigzag chain formed through interconnection of ZnCl_2 units and 4,4'-bpy ligands. As shown in Figure 4, each Zn^{II} is coordinated by two nitrogen atoms from different 4,4'-bpy and two terminal Cl^- ligands in a distorted tetrahedral coordination environment. The $\text{Zn}-\text{N}$ bond lengths are 2.041(5) and 2.057(4) Å, slightly shorter than those in **1**. However, the $\text{N}(1)-\text{Zn}-\text{N}(2\text{A})$ bond angle of $102.93(19)^\circ$ is larger than that in **1**. All the 4,4'-bpy ligands behave in an *exo*-bidentate mode and lie on the same side of the polymer chain. The pyridyl rings are twisted with respect to their corresponding linking phenyl rings, with the dihedral angles between them being 20.8 and 44.6° , respectively. The twisting angle of 76.2° between two phenyl rings about the central bond is smaller than those in **1** and **2**, which means that 4,4'-bpy connects the ZnCl_2 units into a one-dimensional polymeric chain instead of a macrocycle. The adjacent $\text{Zn}\cdots\text{Zn}$ separation bridged by 4,4'-bpy is 11.580 Å. It should be emphasized that there are significant $\pi-\pi$ interactions between a pyridyl ring and the adjacent



Figure 5. View of $\pi-\pi$ interactions between the adjacent chains along the c axis in **3**

equivalent pyridyl rings from another chain (Figure 5); they are approximately parallel, with the dihedral angle between them being 12.9° and the distance between their centroids being 3.817 Å (Figure 6).^[30] There are no other noteworthy weak interactions between the adjacent chains.

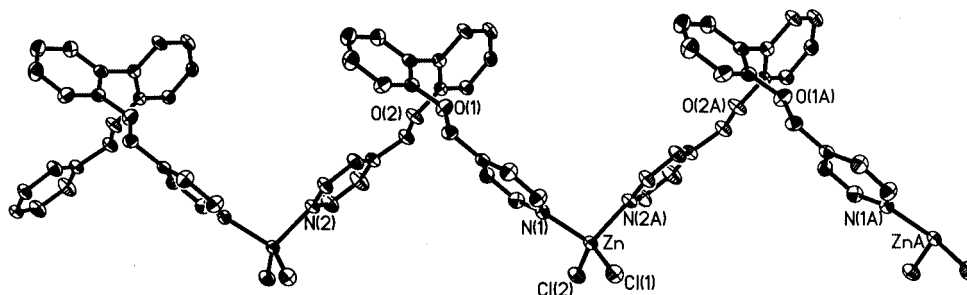


Figure 4. View of the one-dimensional polymeric chain in **3** with the thermal ellipsoids at 30% probability level

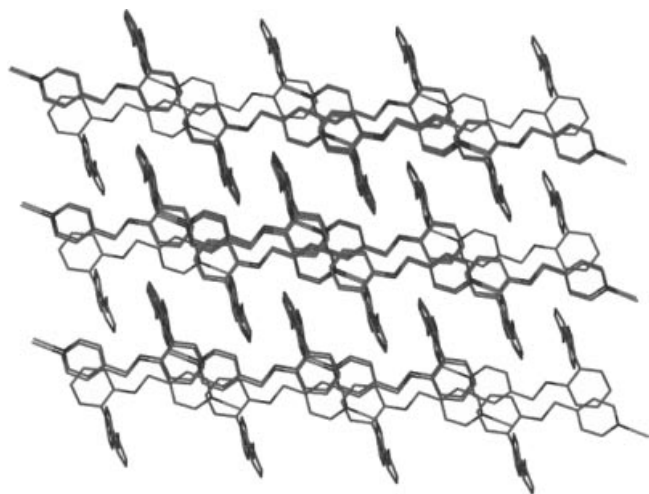


Figure 6. View of the packing structure along the *b* axis in complex **3**

[Zn(4,4'-bpp)Br₂]_n (**4**)

Compounds **3** and **4** are isomorphous. Zn^{II} is coordinated by two nitrogen atoms from different 4,4'-bpp and two terminal Br[−] ligands in a distorted tetrahedral geometry. The Zn–N bond lengths and the N–Zn–N bond angles are 2.052(7)–2.069(7) Å and 101.5(1)°, respectively, similar to those in **3**. The Zn–Br bond lengths of 2.3512(15)–2.3560(13) Å and the Br(1)–Zn–Br(2) bond angle of 119.90(6)° are slightly smaller than their counterparts in **2**. An *exo*-bidentate 4,4'-bpp ligand bridges a pair of adjacent Zn^{II} centers on the same side forming a one-dimensional zigzag chain. The Zn...Zn separation bridged by 4,4'-bpp is 11.688 Å; π – π interaction between the pyridyl ring and an adjacent pyridyl ring from another chain stacks the polymeric chains into a network architecture (Figure 7).

[Co(4,4'-bpp)₂(SCN)₂]_n (**5**)

The single-crystal X-ray diffraction analysis reveals that **5** is a two-dimensional polymer consisting of folded rectangular boxes (Figure 8) and zigzag chains (Figure 9) bridged by Co^{II}. As shown in Figure 8, each Co^{II} has a compressed octahedral coordination environment with four pyridyl nitrogen atoms from different 4,4'-bpp situated in the equatorial plane and two *trans*-thiocyanato nitrogen

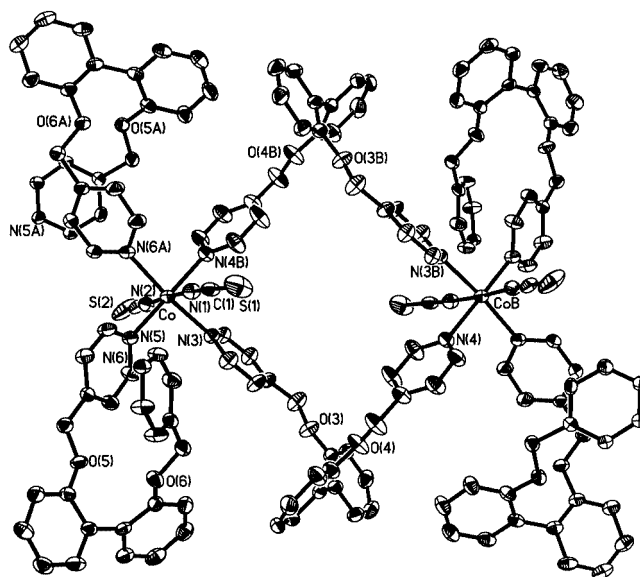


Figure 8. View of the folded rectangular box in **5** with the thermal ellipsoids at 30% probability level

atoms at the axial positions. The four pyridyl units associated with Co^{II} are arranged in a propeller fashion. The Co^{II} is approximately coplanar with the mean plane of four equatorial pyridyl nitrogen atoms, with a deviation of 0.0116 Å towards the axial donor atoms. The Co–N_{py} bond lengths range from 2.162(5) to 2.239(5) Å [av. 2.201(5) Å], which are longer than the Co–N_{NCS} bond lengths of 2.062(5) and 2.080(6) Å [av. 2.071(6) Å]. The SCN[−] groups are almost linear, with N(1)–C(1)–S(1) and N(2)–C(2)–S(2) bond angles of 179.7(6) and 178.6(7)°, respectively. The connections between Co^{II} and SCN[−] groups are slightly bent, with C(1)–N(1)–Co and C(2)–N(2)–Co bond angles of 170.1(6) and 174.7(5)°, respectively, suggesting that the two SCN[−] ligands are not perpendicular to the equatorial plane. Interestingly, there are two independent 4,4'-bpp ligands in this complex, one bridges two Co^{II} centers forming a folded rectangular box of two planes.^[24] The Co...Co separation within the box is 11.446 Å. This type of box is similar to that constructed by dipyrindyl ligands with a 1,1'-bi-2-naphthol connector and [Pt(dppp)(OSO₂CF₃)₂]^[24] [dppp = 1,3-bis(diphenylphosphanyl)propane] and very different from the common rectangular boxes derived from other *exo*-bidentate pyridyl-

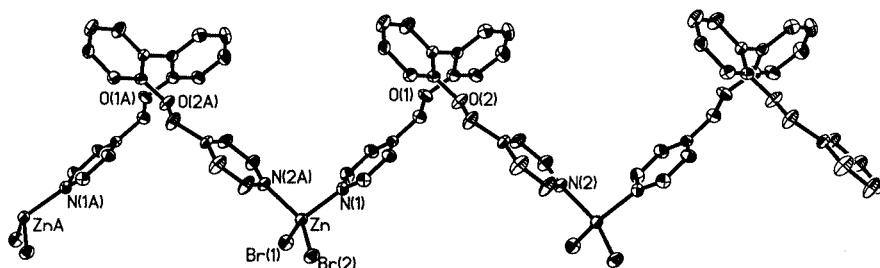
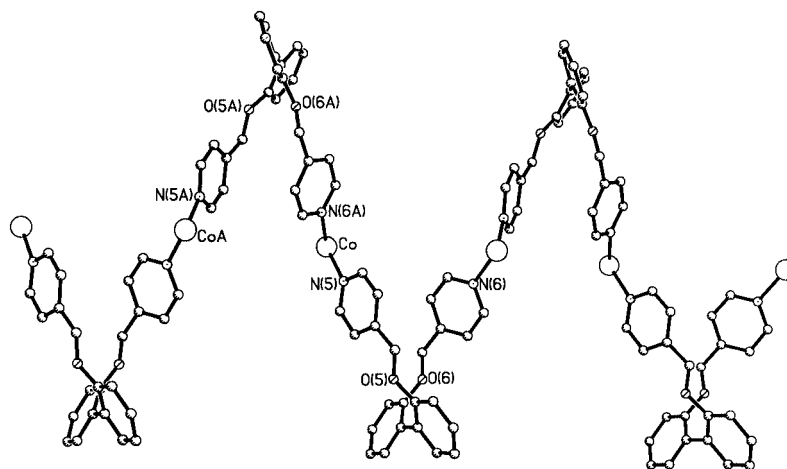
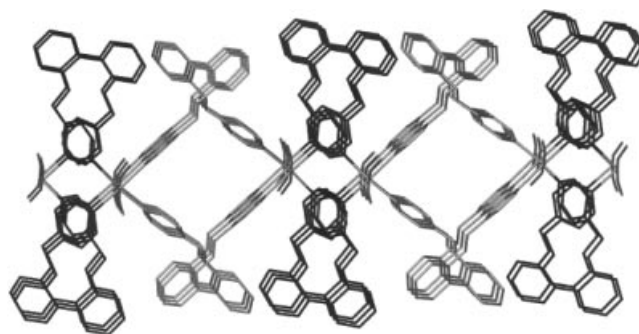
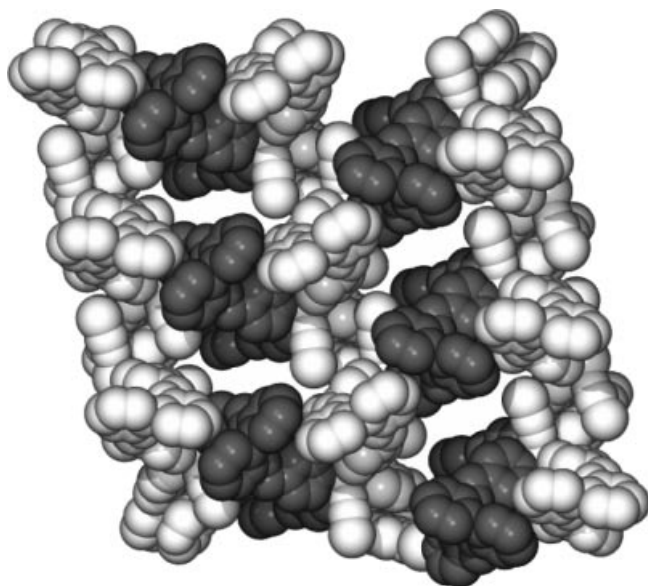


Figure 7. View of the one-dimensional polymeric chain in **4** with the thermal ellipsoids at 30% probability level

Figure 9. View of the zigzag chains in **5**

containing ligands.^[31] In the 4,4'-bpy ligand the dihedral angle between the two phenyl rings is 65.6°. The dihedral angle of 50.8° between the two phenyl rings in the other independent 4,4'-bpy unit is smaller than that in the former and those in complexes **3** and **4**, which results in 4,4'-bpy linking two adjacent Co^{II} into a one-dimensional zigzag chain. Different from **3** and **4**, the 4,4'-bpy ligands lie on different sides of the zigzag chain. The closest Co...Co separation in the zigzag chain is 8.032 Å, which is much shorter than those in the zigzag chains of **3** and **4**. The most intriguing feature in **5** is that rectangular boxes and zigzag chains are fused into a two-dimensional polymer through Co(NCS)₂ units (Figure 10). To the best of our knowledge, this type of complex containing folded rectangular boxes and zigzag chains is unprecedented, which suggests that the

distortion of the biphenyl connector has a great effect on the construction of novel structural motifs (Figure 11).

Figure 11. The packing structure along the *b* axis in **5** showing the linkage of the folded rectangular boxes and zigzag chainsFigure 10. The two-dimensional structure formed by the folded rectangular boxes and zigzag chains in **5**

[{Cd(4,4'-bpy)₂(SCN)₂}·2H₂O]_n (**6**)

Complex **6** is a polycatenated species^[6] whose structure is made up of inclined interpenetrated two-dimensional layers. Each layer is composed of an alternating assembly of left-hand (*M*) and right-hand (*P*) cylindrical 2₁ helices along the *b* axis.^[32] As shown in Figure 12, the coordination sphere of Cd^{II} is defined by four pyridyl nitrogen atoms from different 4,4'-bpy ligands situated in the equatorial plane and two *trans*-thiocyanato nitrogen atoms at the axial positions, resulting in a compressed octahedral coordination environment. The Cd^{II} is displaced 0.0240 Å out of the equatorial plane. The Cd–N_{py} and Cd–N_{SCN} bond lengths are in the range 2.379(5)–2.405(5) Å [av. 2.390(5) Å] and 2.308(7)–2.329(6) Å [av. 2.319(7) Å], respectively. The SCN[−] groups are almost linear, with N(1)–C(1)–S(1) and N(2)–C(2)–S(2) bond angles of 177.9(9) and 174.0(8)°, respectively. The two SCN[−] groups are not perpendicular to the equatorial plane and the C(1)–N(1)–Cd and C(2)–N(2)–Cd bond angles are 135.3(6) and 139.6(6)°,

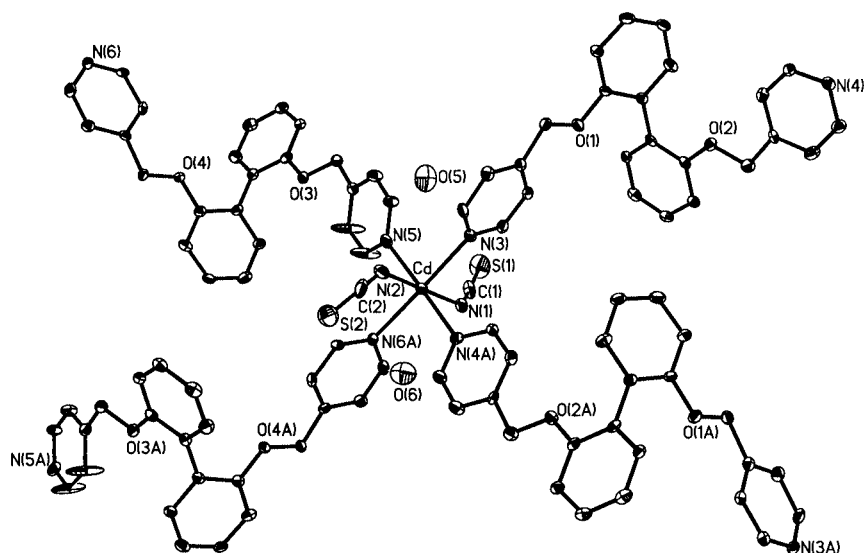


Figure 12. View of the coordination environment of Cd^{II} in **6** with the thermal ellipsoids at 30% probability level

respectively. These values are similar to those in complex **5**. It should be emphasized that there are two independent 4,4'-bpp ligands in this complex, one of which bridges six-coordinate Cd^{II} forming an (*M*) helical column (Figure 13). The repeating period in the helical column is 17.050 Å, which is slightly longer than the $\text{Cd}\cdots\text{Cd}$ distance bridged by 4,4'-bpp (16.590 Å). In the 4,4'-bpp ligand the dihedral

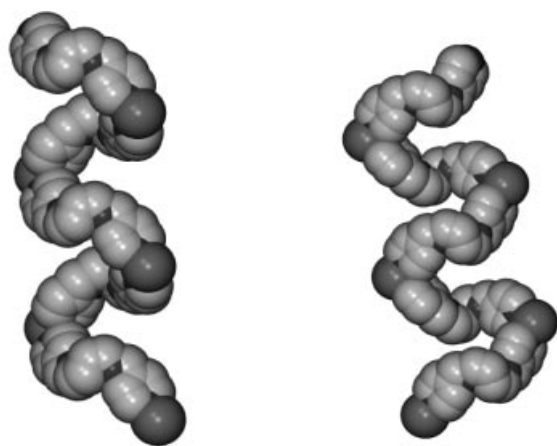


Figure 13. View of the left-hand and right-hand cylindrical 2_1 helices in **6** with uncoordinated water molecules omitted for clarity

angles between phenyl rings and their corresponding linking pyridyl rings are 23.3 and 6.0°, respectively. A drastic twisting is observed between two phenyl rings, with a dihedral angle of 116.9°, which is much larger than those in **3–5** and leads to the formation of the helical column. Interestingly, the other *cis* ligand coordinates to Cd^{II} and forms a (*P*) helical column (Figure 13). The distance of the helical pitch and $\text{Cd}\cdots\text{Cd}$ separation bridged by 4,4'-bpp are 17.050 and 16.668 Å, respectively. In the 4,4'-bpp ligand the dihedral angles between the two phenyl rings as well as between the phenyl rings and their corresponding linking pyridyl rings are 118.1, 32.9 and 10.9°, respectively, which are slightly different from the other 4,4'-bpp ligand. These two types of cylindrical columns are alternatively connected, with the $\text{Cd}(\text{SCN})_2$ units functioning as hinges, forming a unique two-dimensional layer structure (Figures 14 and 15). It should be emphasized that the longer helical pitch and the 4,4'-bpp ligands result in the formation of larger void cavities in the two-dimensional network, which greatly exceeds that required to accommodate the guest molecules in the reaction system. Thus, instead of forming an open, microporous structure, the potential voids are filled by mutually inclined interpenetration of identical two-dimensional frameworks (Figure 16). Uncoordinated water molecules act as guest molecules and further fill in its space.

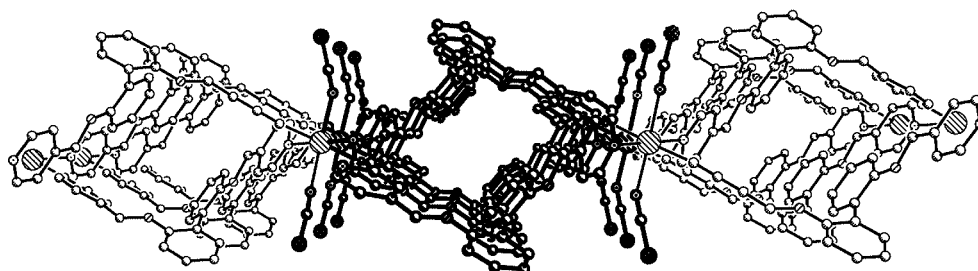


Figure 14. View of the two-dimensional layer along the *b* axis in **6** with uncoordinated water molecules omitted for clarity

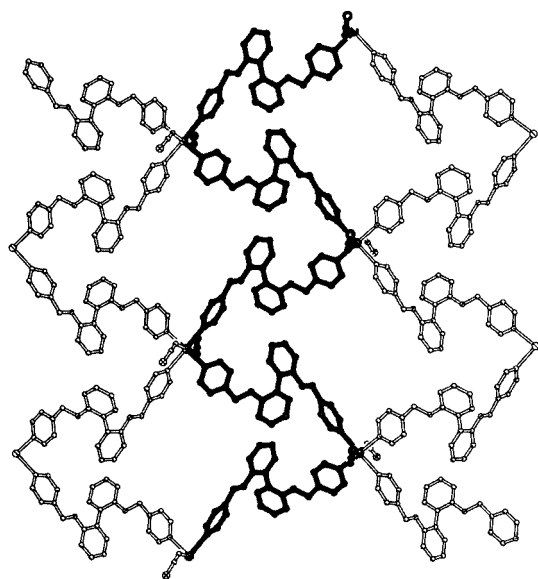


Figure 15. Packing structure along the *c* axis in **6** with uncoordinated water molecules omitted for clarity

Although there have been many helical coordination polymers reported, to the best of our knowledge this type of helix-assembled polycatenated motif is unprecedented.

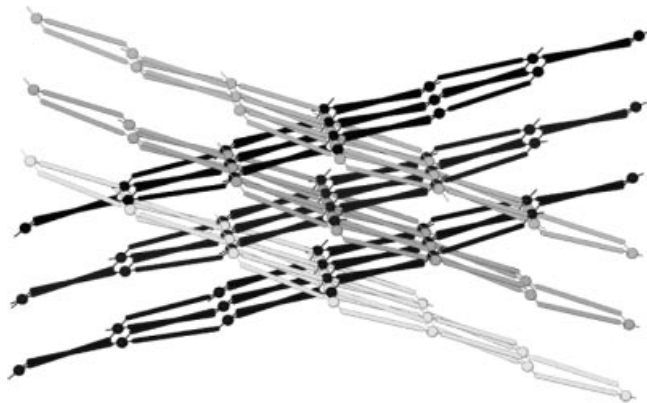


Figure 16. Packing structure of the inclined interpenetrating two-dimensional layers in **6** with partial atoms omitted for clarity

[Cd(4,4'-bpp)(dca)₂]_n (**7**)

Complex **7** consists of two-dimensional Cd(dca)₂ layers bridged by 4,4'-bpp ligands. As shown in Figure 17, Cd^{II} is coordinated by six nitrogen atoms in a distorted octahedral geometry, in which four nitrogen atoms from different dca[−] ligands form the equatorial plane, and two pyridyl nitrogen atoms from different 4,4'-bpp occupy the apical positions. The Cd–N_{dca} and Cd–N_{py} bond lengths are in the range 2.317(6)–2.475(7) Å [av. 2.367(7) Å] and 2.321(6)–2.352(7) Å [av. 2.337(7) Å], respectively; dca[−] has two distinctly different bridging modes: one adopts a usual end-to-end μ-1,5 bridging mode,^[27] and the other acts as a rare μ-1,3 bridge through a terminal nitrile nitrogen atom and the middle nitrogen atom.^[28] These two types of dca[−] bridge Cd^{II} to form a neutral two-dimensional layer structure (Figure 18). The Cd...Cd separations bridged by μ-1,5- and μ-1,3-dca[−] are 7.725 and 6.050 Å, respectively. The 4,4'-bpp ligand acts as an *exo*-bidentate ligand; the dihedral angle between two phenyl rings is 131.6°. However, the dihedral angles between the phenyl rings and their corresponding linking pyridyl rings are 10.1 and 19.1°, respectively. As a result, the 4,4'-bpp ligands are situated at two sides of the layers to saturate the six-coordinate Cd^{II} center and connect the Cd–dca layers into a three-dimensional network. It is note-

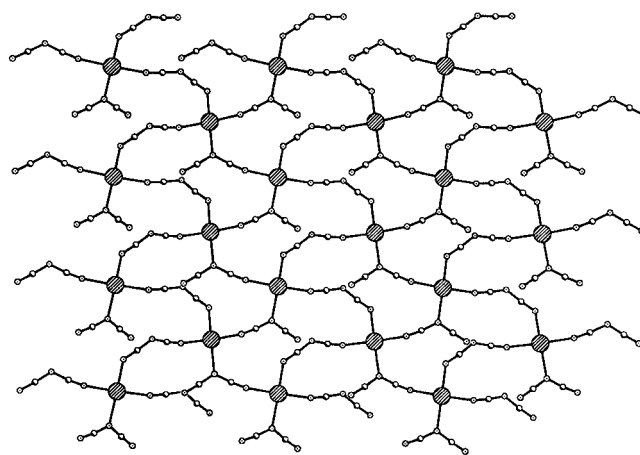


Figure 18. The two-dimensional layer formed by dca[−] and Cd^{II} along the *c* axis in **7**

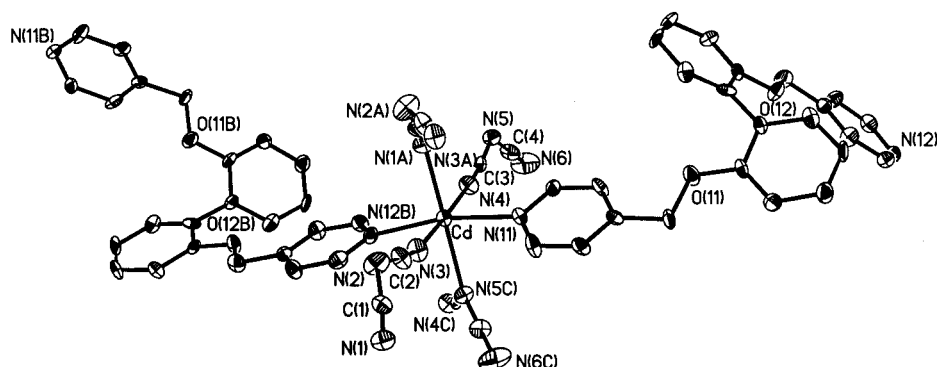


Figure 17. View of the coordination environment of Cd^{II} in **7** with the thermal ellipsoids at 30% probability level

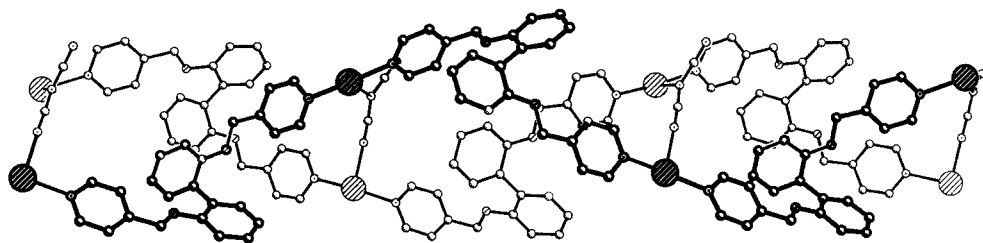


Figure 19. (*M*)- (light) and (*P*)-Cd(4,4'-bpb) (dark) helical chains bridged by μ -1,3-dca in **7**

worthy that the 4,4'-bpb ligands bridge Cd^{II} to form (*M*) and (*P*) helical chains (Figure 19). Different from **6**, the adjacent (*M*) and (*P*) helical chains are connected by μ -1,3-dca ligands instead of metal centers. The distance of the helical pitch and $\text{Cd}\cdots\text{Cd}$ distance bridged by 4,4'-bpb are 29.629 and 15.697 Å, respectively. Hence, complex **7** can be regarded as the fusion of two-dimensional $\text{Cd}(\text{dca})_2$ layers with (*M*)- and (*P*)-Cd(4,4'-bpb) helical chains through Cd^{II} centers (Figure 20).

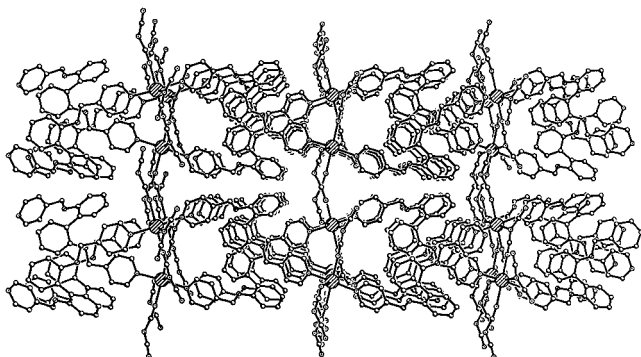


Figure 20. Packing structure along the *a* axis in **7** showing the linkage of the helical chains and the two-dimensional layer

It should be interesting and essential to compare the related structural data of 3,3'-bpb and 4,4'-bpb in complexes **1–7**. As suggested in Table 1, the twisting angles of the biphenyl connector about the central bond in 3,3'-bpb and

4,4'-bpb are responsible for the formation of the structural motifs. Owing to the steric hindrance from the relative orientation of the coordination sites in the pyridyl rings, 3,3'-bpb and 4,4'-bpb bridge ZnCl_2 or ZnBr_2 units generating metallomacrocycles and one-dimensional zigzag chains with 4,4'-bpb at the same sides, respectively. The distortion angles of the biphenyl connector in 3,3'-bpb (130.5° for **1** and 130.2° for **2**) are much larger than those in 4,4'-bpb (76.2° for **3** and 79.6° for **4**); however, the distortion angles of the biphenyl connector of 50.8 and 65.6° in 4,4'-bpb in **5**, which are smaller than those in the polymeric chains of **3** and **4**, lead to the formation of a one-dimensional zigzag chain with 4,4'-bpb at two sides and a folded rectangular box, respectively. When the distortion angles of the biphenyl connector in 4,4'-bpb increase to 116.9 and 118.1°, cylindrical 2_1 helical structures are generated. The largest distortion angle of the biphenyl connector in 4,4'-bpb (131.6°) results in a one-dimensional helical chain in complex **7**. Correspondingly, the dihedral angles between the phenyl rings and linking pyridyl rings are different in each type of structural motif. In the zigzag chain with 4,4'-bpb at two sides, the smallest twisting angle of the biphenyl connector in 4,4'-bpb (50.8°) results in the shortest distance between the metal centers bridged by 4,4'-bpb (8.032 Å) in **5**; the longest distance is found in the right-handed cylindrical 2_1 helix (16.668 Å) of complex **6**. It should be emphasized that the two phenyl rings in free 4,4'-bpb can rotate freely about the central bond, but the rotation is restricted in metal-organic complexes because of pyridyl-*N* coordination; consequently, this restricted rotation gives rise to two confor-

Table 1. Comparison of the structural data from 3,3'-bpb or 4,4'-bpb in **1–7**

Compound	Ligand	Dihedral angles [°]			Distance between metal centers bridged by ligand [Å]	Structure
		[a]	[b]	[c]		
1	3,3'-bpb	130.5	24.7 and 26.5	83.2	14.015	dimetallomacrocycle
2	3,3'-bpb	130.2	26.1 and 28.5	81.0	14.113	dimetallomacrocycle
3	4,4'-bpb	76.2	20.8 and 44.6	76.0	11.580	1D polymeric chain
4	4,4'-bpb	79.6	15.1 and 42.8	77.7	11.688	1D polymeric chain
5	4,4'-bpb	65.6	21.6 and 45.3	74.9	11.446	folded rectangular box
	4,4'-bpb	50.8	24.1 and 49.5	77.4	8.032	1D zigzag chain
6	4,4'-bpb	116.9	23.3 and 6.0	80.8	16.590	(<i>M</i>) cylindrical 2_1 helix
	4,4'-bpb	118.1	32.9 and 10.9	89.3	16.668	(<i>P</i>) cylindrical 2_1 helix
7	4,4'-bpb	131.6	10.1 and 19.1	18.6	15.697	1D helical chain

[a] Biphenyl connector in the ligand. [b] Between the phenyl ring and the corresponding linking pyridyl ring. [c] Between two pyridyl rings at the metal center.

mations [(*M*) and (*P*)] in complexes **6** and **7**.^[22] Therefore, the flexibility of ligands, the coordination propensity of metal ions and the secondary ligands play important roles in the formation of the final networks, meaning that the structural topologies of complexes **5**, **6**, and **7** are unusual.

Conclusions

Seven novel metal-organic complexes containing the flexible dipyridyl ligands 2,2'-bis(3-pyridylmethylenoxy)-1,1'-biphenylene (3,3'-bpp) and 2,2'-bis(4-pyridylmethylenoxy)-1,1'-biphenylene (4,4'-bpp) have been prepared and structurally characterized. In complexes **1–4**, *exo*-bidentate 3,3'-bpp and 4,4'-bpp ligands link ZnX_2 ($\text{X} = \text{Cl}^-$ and Br^-) units into dinuclear metallomacrocycles and one-dimensional zigzag chains, respectively, in which the metal centers adopt a distorted tetrahedral geometry. This reveals that the relative orientation of the nitrogen donors in the pyridyl rings has a great influence on the construction of the supramolecular architectures. The metal centers in both **5** and **6** all have a compressed octahedral geometry, although $\text{Co}(\text{SCN})_2$ and $\text{Cd}(\text{SCN})_2$ hinges fuse one-dimensional zigzag chains and folded rectangular boxes as well as left-handed and right-handed cylindrical 2_1 helices into two distinctly different two-dimensional networks. The topological differences in complexes **3–6** are attributed to the different geometric requirement of the metal ions. The results of structural analyses of **3–6** containing 4,4'-bpp reveal that their structures mainly depend on the geometric requirement of the metal ions and are not influenced greatly by the counteranions, which only act as terminal ligands. The introduction of bridging dca^- counteranions into the reaction system produces a three-dimensional complex **7**, in which 4,4'-bpp functions as a bridge between the adjacent Cd-dca layers. Such differences in **1–7** are realized through the distortion of the biphenyl connector in 3,3'-bpp and 4,4'-bpp. In summary, this research shows that assembly of dipyridyl ligands with a biphenyl connector and metal ions can generate unique structural motifs, which cannot be obtained using normal rigid or flexible *exo*-bidentate organic ligands, such as 4,4'-bipy and related organic ligands. In this regard, we are currently using these results as probes for axial chiral ligands derived from 1,1'-bi-2-naphthol and extending our research to prepare chiral supramolecular species.

Experimental Section

General: 2,2'-Biphenol, 3-picolyl chloride hydrochloride and 4-picolyl chloride hydrochloride were purchased from Acros. All other chemicals are commercially available and were used as purchased without further purification. The NMR spectra were recorded with a Varian Inova-500 spectrophotometer at room temperature and the chemical shifts are quoted in δ (ppm) relative to the deuterated solvent used. The mass spectra were recorded in the Mass Spectrometry Laboratory of the Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University with

a Fisons VG platform. The IR spectra as KBr disks were recorded with a Magna 750 FT-IR spectrophotometer. C, H and N elemental analyses were determined with an Elementary Vario ELIII elemental analyzer.

Synthesis of 3,3'-bpp: A mixture of 2,2'-biphenol (1.86 g, 10 mmol), 3-picolyl chloride hydrochloride (3.61 g, 22 mmol) and NaOH (1.76 g, 44 mmol) in acetone (50 mL) was stirred at reflux under nitrogen for 3 d. After cooling to room temperature, the inorganic salt was removed by filtration and washed with acetone several times. The combined solutions were concentrated under reduced pressure and the red residue was dissolved in ethyl acetate and then washed twice with water and once with brine. The organic layer was dried with anhydrous Na_2SO_4 and filtered. After removal of the solvent under reduced pressure, the residue was purified by chromatography on silica gel to afford a colorless solid. Yield: 3.24 g (88% based on 2,2'-biphenol). ^1H NMR (500 MHz, CDCl_3): δ = 8.44 (d, J = 3.0 Hz, 2 H, H^2), 8.38 (s, 2 H, H^1), 7.40 (d, J = 7.5 Hz, 2 H, H^4), 7.30–7.34 (m, 2 H, H^3), 7.29 (d, J = 1.5 Hz, 2 H, H^9), 7.04–7.11 (m, 4 H, H^7 , H^8), 7.00 (d, J = 8.5 Hz, 2 H, H^6), 4.96 (s, 4 H, H^5) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ = 155.6 (C^7), 148.7 (C^1), 148.0 (C^2), 134.4 (C^4), 132.7 (C^5), 131.4 (C^{12}), 128.7 (C^9 , C^{11}), 123.1 (C^3), 121.2 (C^{10}), 112.9 (C^8), 67.9 (C^6) ppm. ES-MS: m/z = 368 [$\text{M}^+ + 1$]. HRMS: calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2$ [$\text{M}^+ + 1$]; m/z = 368.4342; found 368.4345.

Synthesis of 4,4'-bpp: The procedure was similar to the synthesis of 3,3'-bpp except that 4-picolyl chloride hydrochloride was used instead of 3-picolyl chloride hydrochloride. Yield: 2.75 g (75% based on 2,2'-biphenol). ^1H NMR (500 MHz, CDCl_3): δ = 8.37 (d, J = 6.0 Hz, 4 H, H^1), 7.27 (d, J = 7.5 Hz, 4 H, H^2), 7.04 (d, J = 7.0 Hz, 2 H, H^9), 6.97 (d, J = 5.5 Hz, 4 H, H^6 and H^8), 6.88 (d, J = 7.5 Hz, 2 H, H^7), 4.92 (s, 4 H, H^5) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ = 155.7 (C^5), 149.8 (C^1), 146.6 (C^3), 131.7 (C^7), 129.0 (C^{10}), 128.5 (C^9), 121.5 (C^8), 121.0 (C^2), 112.6 (C^6), 68.5 (C^4) ppm. ES-MS: m/z = 368 [$\text{M}^+ + 1$]. HRMS: calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2$ [$\text{M}^+ + 1$]; m/z = 368.4342; found 368.4349.

Synthesis of $[\text{Zn}_2(3,3'\text{-bpp})_2\text{Cl}_4]$ (1**):** A solution of ZnCl_2 (0.034 g, 0.25 mmol) in H_2O (10 mL) was slowly added to a stirring solution of 4,4'-bpp (0.092 g, 0.25 mmol) in MeOH (10 mL) to give a white precipitate. The reaction mixture was heated to 60 °C and DMF was added dropwise (about 1 mL) until the precipitate dissolved. The resulting solution was filtered and kept in air at room temperature for two weeks. Colorless crystals of **1** suitable for X-ray diffraction were obtained. Yield: 0.08 g (63%). $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}_2\text{Zn}$ (504.69): calcd. C 57.11, H 3.96, N 5.55; found C 57.09, H 4.98, N 5.57. ^1H NMR (500 MHz, CDCl_3): δ = 8.44 (s, 4 H), 8.42 (s, 4 H), 7.58 (d, J = 7.5 Hz, 4 H), 7.33 (t, J = 7.5 Hz, 15 Hz, 4 H), 7.27–7.29 (m, 4 H), 7.23 (dd, J = 2.0, 7.5 Hz, 4 H), 7.16 (d, J = 8.0 Hz, 4 H), 7.02 (t, J = 7.0 Hz, 14 Hz, 4 H), 5.10 (s, 8 H) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3121 cm^{-1} (vw), 3047 (w), 2913 (vw), 2858 (w), 1614 (m), 1593 (m), 1564 (w), 1504 (w), 1482 (s), 1456 (m), 1436 (s), 1431 (s), 1387 (m), 1335 (w), 1265 (s), 1234 (s), 1194 (m), 1163 (w), 1125 (s), 1057 (m), 1032 (s), 1002 (m), 933 (vw), 867 (w), 814 (w), 796 (m), 766 (s), 697 (m), 658 (m), 642 (w), 613 (vw), 540 (vw), 486 (vw), 453 (vw).

Synthesis of $[\text{Zn}_2(3,3'\text{-bpp})_2\text{Br}_4]$ (2**):** The procedure was similar to the synthesis of complex **1** except that ZnBr_2 (0.056 g, 0.25 mmol) was used instead of ZnCl_2 . Yield: 0.10 g (67%). $\text{C}_{24}\text{H}_{20}\text{Br}_2\text{N}_2\text{O}_2\text{Zn}$ (593.61): calcd. C 48.56, H 3.37, N 4.72; found C 48.52, H 3.40, N 4.70. ^1H NMR (500 MHz, CDCl_3): δ = 8.44 (s, 4 H), 8.43 (s, 4 H), 7.58 (d, J = 7.0 Hz, 4 H), 7.33 (t, J = 8.5 Hz, 17 Hz, 4 H), 7.28–7.31 (m, 4 H), 7.23 (d, J = 6.0 Hz, 4 H), 7.16 (d, J = 7.0 Hz,

4 H), 7.02 (t, $J = 7.0$ Hz, 14 Hz, 4 H), 5.10 (s, 8 H) ppm. IR (KBr pellet): $\tilde{\nu} = 3121$ cm $^{-1}$ (vw), 3045 (w), 2910 (w), 2858 (w), 1614 (m), 1595 (m), 1563 (vw), 1504 (w), 1483 (s), 1458 (m), 1437 (s), 1385 (m), 1335 (w), 1284 (w), 1263 (s), 1232 (s), 1194 (m), 1165 (w), 1124 (s), 1057 (m), 1034 (s), 1020 (m), 1001 (m), 933 (vw), 912 (vw), 866 (w), 793 (m), 764 (s), 698 (s), 658 (m), 615 (vw), 544 (vw), 486 (vw), 454 (vw).

Synthesis of [Zn(4,4'-bpb)Cl $_2$] $_n$ (3): A solution of 4,4'-bpb (0.037 g, 0.1 mmol) in MeOH (5 mL) was carefully layered on top of a solution of ZnCl $_2$ (0.014 g, 0.1 mmol) in H $_2$ O (5 mL). Diffusion between the two phases over a period of two weeks produced colorless crystals. Yield: 0.04 g (79%). C $_{24}$ H $_{20}$ Cl $_2$ N $_2$ O $_2$ Zn (504.69): calcd. C 57.11, H 3.96, N 5.55; found C 57.07, H 4.02, N 5.53. IR (KBr pellet): $\tilde{\nu} = 3121$ cm $^{-1}$ (vw), 3052 (w), 2916 (w), 2852 (w), 1624 (s), 1593(m), 1563 (w), 1504 (m), 1481 (m), 1450 (s), 1436 (s), 1390 (m), 1329 (vw), 1306 (m), 1265 (s), 1234 (s), 1163 (vw), 1121 (m), 1057 (m), 1032 (s), 1005 (w), 933 (vw), 866 (w), 814 (s), 786 (m), 752 (s), 642 (w), 613 (vw), 486 (w), 453 (vw).

Synthesis of [Zn(4,4'-bpb)Br $_2$] $_n$ (4): The procedure was similar to the synthesis of complex 3 except that ZnBr $_2$ (0.023 g, 0.1 mmol) was used instead of ZnCl $_2$. Yield: 0.05 g (84%). C $_{24}$ H $_{20}$ Br $_2$ N $_2$ O $_2$ Zn (593.61): calcd. C 48.56, H 3.37, N 4.72; found C 48.51, H 3.39, N 4.68. IR (KBr pellet): $\tilde{\nu} = 3121$ cm $^{-1}$ (vw), 3062 (w), 2910 (w), 2856 (w), 1624 (s), 1593 (m), 1563 (w), 1504 (s), 1481 (s), 1440 (s), 1431 (s), 1387 (s), 1328 (w), 1284 (s), 1267 (s), 1234 (s), 1158 (w), 1121 (s), 1056 (s), 1030 (s), 1005 (m), 933 (vw), 912 (vw), 864 (w), 829 (w), 810 (s), 770 (s), 750 (s), 717 (w), 641 (m), 613 (vw), 544 (vw), 513 (vw), 486 (w), 454 (w).

Synthesis of [Co(4,4'-bpb) $_2$ (SCN) $_2$] $_n$ (5): The procedure was similar to the synthesis of complex 3 except that Co(NO $_3$) $_2$ ·6H $_2$ O (0.029 g, 0.1 mmol) and NH $_4$ SCN (0.015 g, 0.2 mmol) were used instead of ZnCl $_2$. Yield: 0.04 g (88% based on 4,4'-bpb). C $_{50}$ H $_{40}$ CoN $_6$ O $_4$ S $_2$ (911.93): calcd. C 65.85, H 4.39, N 9.21; found C 65.82, H 4.42, N 9.18. IR (KBr pellet): $\tilde{\nu} = 3423$ cm $^{-1}$ (w), 3064 (w), 2914 (w), 2854 (w), 2075 (vs), 1618 (s), 1595 (m), 1564 (w), 1504 (m), 1483 (m), 1441 (s), 1421 (s), 1385 (m), 1325 (w), 1271 (s), 1225 (s), 1163 (vw), 1113 (m), 1057 (m), 1016 (m), 939 (vw), 810 (m), 762 (s), 634 (w), 618 (vw), 494 (w).

Synthesis of [Cd(4,4'-bpb) $_2$ (SCN) $_2$ ·2H $_2$ O] $_n$ (6): The procedure was similar to the synthesis of complex 3 except that Cd(NO $_3$) $_2$ ·6H $_2$ O (0.031 g, 0.1 mmol) and NH $_4$ SCN (0.015 g, 0.2 mmol) were used instead of ZnCl $_2$. Yield: 0.04 g (80% based on 4,4'-bpb). C $_{50}$ H $_{44}$ CdN $_6$ O $_6$ S $_2$ (1001.4): calcd. C 59.96, H 4.39, N 8.39; found C 59.91, H 4.37, N 8.32%. IR (KBr pellet): $\tilde{\nu} = 3435$ cm $^{-1}$ (w), 3120 (w), 2914 (w), 2852 (w), 2033 (vs), 1615 (s), 1596 (m), 1562 (w), 1504 (w), 1479 (m), 1436 (s), 1423 (s), 1399 (m), 1324 (vw), 1269 (m), 1231 (s), 1161 (vw), 1126 (m), 1062 (m), 1013 (m), 939 (vw), 814 (m), 751 (m), 635 (w), 619 (vw), 486 (w).

Synthesis of [Cd(4,4'-bpb)(dca) $_2$] $_n$ (7): The procedure was similar to the synthesis of complex 3 except that Cd(NO $_3$) $_2$ ·4H $_2$ O (0.031 g, 0.1 mmol) and Na(dca) $_2$ (0.018 g, 0.2 mmol) were used instead of ZnCl $_2$. Yield: 0.05 g (82%). C $_{28}$ H $_{20}$ CdN $_8$ O $_2$ (612.92): calcd. C 54.87, H 3.26, N 18.27; found C 54.85, H 3.29, N 18.25. IR (KBr pellet): $\tilde{\nu} = 3529$ cm $^{-1}$ (w), 3061 (w), 2916 (w), 2891 (w), 2845 (w), 2305 (s), 2258 (s), 2229 (vs), 2170 (vs), 1618 (m), 1597 (w), 1562 (w), 1504 (w), 1479 (m), 1425 (s), 1369 (m), 1327 (w), 1306 (m), 1263 (s), 1252 (s), 1227 (s), 1161 (vw), 1124 (m), 1061 (m), 1018 (m), 933 (w), 816 (s), 802 (m), 756 (s), 638 (w), 613 (vw), 510 (w), 490 (m), 467 (vw).

X-ray Crystallographic Study: Intensity data for complexes 1–7 were measured with a Siemens Smart CCD diffractometer with

Table 2. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for 1–7^[a]

Complex 1			
Zn–N(1)	2.061(4)	Zn–N(2A)	2.070(5)
Zn–Cl(1)	2.2245(17)	Zn–Cl(2)	2.2150(16)
N(1)–Zn–N(2A)	99.53(18)	N(1)–Zn–Cl(2)	108.83(14)
N(2A)–Zn–Cl(2)	105.96(14)	N(1)–Zn–Cl(1)	103.74(14)
N(2A)–Zn–Cl(1)	112.60(14)	Cl(2)–Zn–Cl(1)	123.52(7)
Complex 2			
Zn–N(1)	2.068(8)	Zn–N(2A)	2.085(9)
Zn–Br(1)	2.3614(16)	Zn–Br(2)	2.3674(16)
N(1)–Zn–N(2A)	98.6(3)	N(1)–Zn–Br(1)	108.7(2)
N(2A)–Zn–Br(1)	106.9(2)	N(1)–Zn–Br(2)	105.1(2)
N(2A)–Zn–Br(2)	113.0(2)	Br(1)–Zn–Br(2)	121.92(6)
Complex 3			
Zn–N(1)	2.041(5)	Zn–N(2A)	2.057(4)
Zn–Cl(1)	2.2155(17)	Zn–Cl(2)	2.2153(16)
N(1)–Zn–N(2A)	102.93(19)	N(1)–Zn–Cl(2)	108.90(14)
N(2A)–Zn–Cl(2)	108.58(14)	N(1)–Zn–Cl(1)	108.01(14)
N(2A)–Zn–Cl(1)	106.27(14)	Cl(2)–Zn–Cl(1)	120.71(7)
Complex 4			
Zn–N(1)	2.052(7)	Zn–N(2A)	2.069(7)
Zn–Br(1)	2.3512(15)	Zn–Br(2)	2.3560(13)
N(1)–Zn–N(2A)	101.8(3)	N(1)–Zn–Br(1)	108.1(2)
N(2A)–Zn–Br(1)	107.9(2)	N(1)–Zn–Br(2)	109.5(2)
N(2A)–Zn–Br(2)	108.1(2)	Br(1)–Zn–Br(2)	119.90(6)
Complex 5			
Co–N(1)	2.062(5)	Co–N(2)	2.080(6)
Co–N(5)	2.162(5)	Co–N(6A)	2.181(5)
Co–N(3)	2.222(5)	Co–N(4B)	2.239(5)
N(1)–Co–N(2)	176.6(2)	N(1)–Co–N(5)	87.1(2)
N(2)–Co–N(5)	92.15(19)	N(1)–Co–N(6A)	93.8(2)
N(2)–Co–N(6A)	89.53(19)	N(5)–Co–N(6A)	91.94(18)
N(1)–Co–N(3)	89.0(2)	N(2)–Co–N(3)	87.73(19)
N(5)–Co–N(3)	95.59(18)	N(6A)–Co–N(3)	172.08(18)
N(1)–Co–N(4B)	89.1(2)	N(2)–Co–N(4B)	91.78(19)
N(5)–Co–N(4B)	175.97(19)	N(6A)–Co–N(4B)	87.20(19)
N(3)–Co–N(4B)	85.45(19)	C(1)–N(1)–Co	170.1(6)
C(2)–N(2)–Co	174.7(5)	N(1)–C(1)–S(1)	179.7(6)
N(2)–C(2)–S(2)	178.6(7)		
Complex 6			
Cd–N(1)	2.329(6)	Cd–N(2)	2.308(7)
Cd–N(3)	2.384(5)	Cd–N(4B)	2.405(5)
Cd–N(5)	2.393(5)	Cd–N(6A)	2.379(5)
N(2)–Cd–N(1)	178.2(2)	N(1)–Cd–N(6A)	90.6(2)
N(1)–Cd–N(3)	89.81(18)	N(1)–Cd–N(5)	88.5(2)
N(1)–Cd–N(4B)	93.37(18)	N(2)–Cd–N(3)	89.22(19)
N(2)–Cd–N(5)	93.0(2)	N(2)–Cd–N(6A)	90.4(2)
N(2)–Cd–N(4B)	85.14(19)	N(3)–Cd–N(5)	90.26(17)
N(3)–Cd–N(4B)	90.17(17)	N(5)–Cd–N(4B)	178.11(19)
N(6A)–Cd–N(4B)	91.37(17)	N(6A)–Cd–N(3)	178.39(17)
N(6A)–Cd–N(5)	88.19(17)	C(1)–N(1)–Cd	135.3(6)
C(2)–N(2)–Cd	139.6(6)	N(1)–C(1)–S(1)	177.9(9)
N(2)–C(2)–S(2)	174.0(8)		

Table 2. (continued)

Complex 7			
Cd–N(4)	2.318(8)	Cd–N(11)	2.322(9)
Cd–N(1A)	2.324(10)	Cd–N(3)	2.334(9)
Cd–N(12B)	2.359(9)	Cd–N(5C)	2.470(10)
N(4)–Cd–N(11)	93.2(3)	N(4)–Cd–N(1A)	90.3(3)
N(11)–Cd–N(1A)	92.9(4)	N(4)–Cd–N(3)	177.3(4)
N(11)–Cd–N(3)	86.2(3)	N(1A)–Cd–N(3)	87.0(3)
N(4)–Cd–N(12B)	92.1(3)	N(11)–Cd–N(12B)	169.0(3)
N(1A)–Cd–N(12B)	96.7(4)	N(3)–Cd–N(12B)	88.9(3)
N(4)–Cd–N(5C)	88.8(3)	N(11)–Cd–N(5C)	88.0(3)
N(1A)–Cd–N(5C)	178.7(3)	N(3)–Cd–N(5C)	93.8(3)
N(12B)–Cd–N(5C)	82.5(3)		

[a] Symmetry code: **1** (A): $-x + 2, -y, -z$; **2** (A): $-x + 1, -y + 1, -z$; **3** (A): $x + 1/2, y + 1/2, z$; **4** (A): $x + 1/2, y + 1/2, z$; **5** (A): $-x, y + 1/2, -z - 1/2$; **5** (B): $-x + 1, -y - 2, -z$; **6** (A): $-x + 2, -y, z + 1/2$; **6** (B): $-x + 1, -y + 1, z + 1/2$; **7** (A): $x + 1/2, -y + 1, z$; **7** (B): $-x + 1, -y, z - 1/2$; **7** (C): $x - 1/2, -y, z$.

graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. All empirical absorption corrections were applied with the SADABS program.^[33] The structures were solved by direct methods^[34] and refined on F^2 by full-matrix least squares using the SHELXL-97 program package.^[35] The positions of H atoms were generated geometrically (C–H bond fixed at $0.96 \text{ \AA}$), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. The selected bond lengths and angles for **1–7** are listed in Table 2. Crystal data and structure determination data for **1–7** are listed in Table 4. CCDC-232662 to -232668 (**1–7**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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- [1] [1a] J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**. [1b] J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, J. Wiley and Sons, New York, **2000**. [2] [2a] S. A. Bourne, J. Lu, A. Mondal, B. Moulton, M. J. Zaworotko, *Angew. Chem. Int. Ed.* **2001**, *40*, 2111–2113. [2b] M. Munakata, L. P. Wu, T. Kuroda-Sowa, *Adv. Inorg. Chem.* **1999**, *46*, 173–303. [3] [3a] M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330. [3b] S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–908. [4] [4a] D. A. Beauchamp, S. J. Loeb, *Chem. Commun.* **2002**, 2484–2485. [4b] D. A. McMoran, P. J. Steel, *Chem. Commun.* **2002**, 2120–2121. [4c] M. Maekawa, H. Konaka, Y. Suenaga, T. Kuroda-Sowa, M. Munakata, *J. Chem. Soc., Dalton Trans.* **2000**, 4160–4166. [5] [5a] O. R. Evan, W. B. Lin, *Acc. Chem. Res.* **2002**, *35*, 511–522 and references cited therein. [5b] C. Janiak, *Dalton Trans.* **2003**, 2781–2804. [6] [6a] L. Carlucci, G. Ciani, D. M. Proserpio, *Cryst. Eng. Commun.* **2003**, *5*, 269–279. [6b] S. O. H. Gutschke, M. Molinier, A. K. Powell, R. E. P. Winpenny, P. T. Wood, *Chem. Commun.* **1996**, 823–824.

- [7] [7a] S. Banfi, L. Carlucci, E. Caruso, G. Ciani, D. M. Proserpio, *J. Chem. Soc., Dalton Trans.* **2002**, 2714–2721. [7b] J. Keegan, P. E. Kruger, M. Nieuwenhuysen, N. Martin, *Cryst. Growth Design* **2002**, *2*, 329–332. [8] [8a] Y. Cui, S. J. Lee, W. Lin, *J. Am. Chem. Soc.* **2003**, *125*, 6014–6015. [8b] D. Braga, M. Polito, M. Braccacini, D. D'Adario, E. Tagliavini, D. M. Proserpio, F. Grepioni, *Chem. Commun.* **2002**, 1081–1082. [8c] J. Schneider, M. Köckerling, R. Koppitzky, G. Henkel, *Eur. J. Inorg. Chem.* **2003**, 1727–1734. [9] [9a] Y. B. Dong, J. Y. Cheng, R. Q. Huang, M. D. Smith, H. C. zur Loye, *Inorg. Chem.* **2003**, *42*, 5699–5706. [9b] M. L. Tong, S. L. Zheng, X. M. Chen, *Chem. Eur. J.* **2000**, *6*, 3729–3738. [10] [10a] O. S. Jung, Y. J. Kim, Y. A. Lee, J. K. Park, H. K. Chae, *J. Am. Chem. Soc.* **2000**, *122*, 9921–9925. [10b] K. A. Hirsch, S. R. Wilson, J. S. Moore, *Inorg. Chem.* **1997**, *36*, 2960–2968. [11] [11a] G. D. Munno, F. Cipriani, D. Armentano, M. Julve, J. A. Real, *New J. Chem.* **2001**, *25*, 1031–1036. [11b] R. W. Saalfrank, I. Bernt, M. M. Chowdhry, F. Hampel, G. B. M. Vaughan, *Chem. Eur. J.* **2001**, *7*, 2765–2769. [12] [12a] O. S. Jung, S. H. Park, K. M. Kim, H. G. Jang, *Inorg. Chem.* **1998**, *37*, 5781–5785. [12b] T. L. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers, M. J. Zaworotko, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 972–973. [13] [13a] A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117–138. [13b] P. J. Hargman, D. Hargman, J. Zubieta, *Angew. Chem. Int. Ed.* **1999**, *38*, 2639–2684. [14] [14a] S. Kitagawa, M. Kondo, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1799–1806. [14b] S. Belanger, J. T. Hupp, C. L. Stern, R. V. Slone, D. F. Watson, T. G. Carrell, *J. Am. Chem. Soc.* **1999**, *121*, 557–558. [15] [15a] K. Biradha, M. Fujita, *J. Chem. Soc., Dalton Trans.* **2000**, 3805–3810. [15b] K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem. Int. Ed.* **2000**, *39*, 3843–3845. [16] [16a] X. H. Bu, W. Chen, S. L. Lu, R. H. Zhang, D. Z. Liao, W. M. Bu, M. Shionoya, F. Brisse, J. Ribas, *Angew. Chem. Int. Ed.* **2001**, *40*, 3201–3203. [16b] F. A. A. Paz, Y. Z. Khimyak, A. D. Bond, J. Rocha, J. Klinowski, *Eur. J. Inorg. Chem.* **2002**, 2823–2828. [16c] W. J. Belcher, C. A. Longstaff, M. R. Neckenig, J. W. Steed, *Chem. Commun.* **2002**, 1602–1603. [17] [17a] P. L. Caradoc-Davies, D. H. Gregory, L. R. Hanton, J. M. Turnbull, *J. Chem. Soc., Dalton Trans.* **2002**, 1574–1580. [17b] D. M. L. Goodgame, D. A. Grachvogel, I. Hussain, A. J. P. White, D. J. Williams, *Inorg. Chem.* **1999**, *38*, 2057–2063 and references cited therein. [18] M. C. Hong, Y. J. Zhao, W. P. Su, R. Cao, M. Fujita, Z. Y. Zhou, A. S. C. Chan, *J. Am. Chem. Soc.* **2000**, *122*, 4819–4820. [19] M. C. Hong, Y. J. Zhao, W. P. Su, R. Cao, M. Fujita, Z. Y. Zhou, A. S. C. Chan, *Angew. Chem. Int. Ed.* **2000**, *39*, 2468–2470. [20] R. H. Wang, M. C. Hong, W. P. Su, Y. C. Liang, R. Cao, Y. J. Zhao, J. B. Weng, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 725–730. [21] M. C. Hong, W. P. Su, R. Cao, M. Fujita, J. X. Lu, *Chem. Eur. J.* **2000**, *6*, 427–432. [22] [22a] R. H. Wang, M. C. Hong, J. H. Luo, R. Cao, J. B. Weng, *Chem. Commun.* **2003**, 1018–1019. [22b] J.-M. Rueff, S. Pillet, N. Clauser, G. Bonaventure, M. Souhassou, P. Rabu, *Eur. J. Inorg. Chem.* **2002**, 895–900. [22c] H. Kumagai, K. Inoue, M. Kurmoo, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1283–1289. [23] [23a] L. Pu, *Chem. Rev.* **1998**, *98*, 2405–2494. [23b] R. H. Wang, L. J. Xu, X. S. Li, Y. M. Li, Q. Shi, Z. Y. Zhou, M. C. Hong, A. S. C. Chan, *Eur. J. Inorg. Chem.* **2004**, 1595–1599. [24] T. W. Kim, M. S. Lah, J. I. Hong, *Chem. Commun.* **2001**, 743–744. [25] [25a] M. Kondo, M. Shimamura, S. Noro, S. Minakoshi, A. Asami, K. Seki, S. Kitagawa, *Chem. Mater.* **2000**, *12*, 1288–1299. [25b] X. M. Ouyang, B. L. Fei, T. Okamura, H. W. Bu, W. Y.

- Sun, W. X. Tang, N. Ueyama, *Eur. J. Inorg. Chem.* **2003**, 618–627. ^[25c] C. Karunakaran, K. R. J. Thomas, A. Shunmugasundaram, R. Murugesan, *J. Mol. Struct.* **2000**, 523, 213–221.
- ^[26] ^[26a] H. P. Wu, C. Janiak, L. Uehlin, P. Klüfers, P. Mayer, *Chem. Commun.* **1998**, 2637–2638. ^[26b] M. Fettouhi, B. E. Ali, A. M. El-Ghanam, S. Golhen, L. Ouahab, N. Daro, J. P. Sutter, *Inorg. Chem.* **2002**, 41, 3705–3712.
- ^[27] ^[27a] S. R. Batten, K. S. Murray, *Coord. Chem. Rev.* **2003**, 246, 103–130. ^[27b] P. Jensen, S. R. Batten, B. Moubaraki, K. S. Murray, *J. Chem. Soc., Dalton Trans.* **2002**, 3712–3722. ^[27c] S. Dalai, P. S. Mukherjee, E. Zangrando, N. R. Chaudhuri, *New J. Chem.* **2002**, 26, 1185–1189. ^[27d] J. L. Manson, A. M. Arif, C. D. Incarvito, L. M. Liable-Sands, A. L. Rheingold, J. S. Miller, *J. Solid State Chem.* **1999**, 145, 369–378.
- ^[28] Z. M. Wang, B. W. Sun, J. Luo, S. Gao, C. S. Liao, C. H. Yan, Y. Li, *Inorg. Chim. Acta* **2002**, 332, 127–134.
- ^[29] ^[29a] C. Klcin, E. Graf, M. W. Hosseini, A. D. Cian, N. Kyritsakas, *Eur. J. Inorg. Chem.* **2003**, 1299–1302. ^[29b] L. Carlucci, G. Ciani, D. M. Proserpio, *J. Chem. Soc., Dalton Trans.* **1999**, 1799–1804. ^[29c] M. Sasa, T. Tanaka, X. H. Bu, M. Shiro, M. Shionoya, *J. Am. Chem. Soc.* **2001**, 123, 10750–10751. ^[29d] R. Burth, H. Vahrenkamp, *Inorg. Chim. Acta* **1998**, 282, 193–201.
- ^[30] C. Janiak, *J. Chem. Soc., Dalton Trans.* **2000**, 3885–3896.
- ^[31] ^[31a] M. Fujita, S. Nago, M. Iida, K. Ogata, K. Ogura, *J. Am. Chem. Soc.* **1993**, 115, 1574–1575. ^[31b] K. Onitsuka, S. Yamamoto, S. Takahashi, *Angew. Chem. Int. Ed.* **1999**, 38, 174–178. ^[31c] C. A. Hunter, L. D. Sarson, *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 2313–2317.
- ^[32] ^[32a] M. Munakata, L. P. Wu, T. Kuroda-Sowa, *Adv. Inorg. Chem.* **1999**, 46, 173–303. ^[32b] V. V. Ponomarova, V. V. Komarchuk, I. Boldog, A. N. Chernega, J. Sieler, K. V. Domasevitch, *Chem. Commun.* **2002**, 436–437. ^[32c] M. Kondo, M. Miyazawa, Y. Irie, R. Shinagawa, T. Horiba, A. Nakamura, T. Naito, K. Maeda, S. Utsuno, F. Uchida, *Chem. Commun.* **2002**, 2156–2157.
- ^[33] G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Göttingen, **1996**.
- ^[34] G. M. Sheldrick, *SHELXS 97, Program for Crystal Structure Solution*, University of Göttingen, Göttingen, **1997**.
- ^[35] G. M. Sheldrick, *SHELXS 97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, **1997**.

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